aldehyde, 5 cc. of water, 2.5 g. of silver nitrate and 1 cc. of methanol, was added dropwise over a 10-minute period a solution of 1.7 g. of potassium hydroxide in 5 cc. of water. The mixture was stirred for 2.5 hours at room temperature. The black silver precipitate which resulted on addition of base to the original solution was filtered, the residue was washed with water, and the water washings were combined with the filtrate. The aqueous basic filtrate was extracted three times with 100-cc. portions of ether to remove any traces of the dialdehyde. The filtrate was then acidified with 6 *N* sulfuric acid to a *p*H of 2–3 and again extracted with three 100-cc. portions of ether. The ether extract was evaporated to dryness at reduced pressure and the white crystalline residue was dissolved in 10 cc. of methanol. Crystallization from methanol yielded 0.1 g. of a white crystalline compound, m.p. 220–221°. A mixed m.p. with *trans*-hexahydrophthalic acid, prepared as described below, gave no depression.

***trans*-Hexahydrophthalic Acid.**[19]—Fumaric acid (5 g.), 25 cc. of water, a trace of *t*-butylcatechol and 5 cc. of butadiene were heated at 135° for 45 minutes in a bomb. The resulting solution was filtered hot through a Filteraid to remove any polymer, and 3.9 g. of product was obtained after the solution stood overnight; recrystallization from water gave material melting at 171–172°. (Alder and Schumacher[23] report a m.p. of 172°.) The product gave a large depression on mixed m.p. with *cis*-Δ^4-tetrahydrophthalic acid.[20,32]

Reduction of the tetrahydro acid with hydrogen and palladium–charcoal, followed by crystallization from hot water, yielded the *trans*-acid, of m.p. 217–221° (Diels and Alder[20] report 215–221°.)

Oxidation of Δ^4-Tetrahydrophthalaldehyde (VIIa) to *cis*-Δ^4-Tetrahydrophthalic Acid.—The oxidation of 1.3 g. of tetrahydrophthalaldehyde ($n^{22}\text{D}$ 1.4942, prepared from the oily maleic dialdehyde and butadiene) with silver oxide was carried out essentially as described above. The ether solution containing the acidic products of oxidation was concentrated, the residue was dissolved in 50 cc. of water and was treated with norite. Concentration to small volume yielded crystalline material, which, after three further crystallizations from water, melted at 169–171° (wt., 0.2 g.) and gave no depression on mixed m.p. with *cis*-Δ^4-tetrahydrophthalic acid; a large depression was observed on mixed m.p. with the *trans*-acid.

Condensation Reaction between Tetrahydrophthalaldehyde and Methoxyacetone; Tetrahydrophthalide.—Tetrahydrophthalaldehyde (6.0 g., VIIa, prepared from oily maleic dialdehyde) and 4.2 cc. of methoxyacetone in 300 cc. of absolute alcohol were treated with a solution of 6 g. of sodium hydroxide in aqueous alcohol. After standing for 36 hours, most of the alcohol was removed *in vacuo*, the residue was dissolved in 250 cc. of water and extracted four times with 200-cc. portions of chloroform. The aqueous layer was acidified and extracted with 250-cc. portions of chloroform. The chloroform from the extraction of the basic solutions was removed at reduced pressure and the residue was dissolved in benzene and chromatographed on alumina. None of the fractions showed a conjugated carbonyl absorption in the ultraviolet.

The chloroform from the extraction of the acidified solution was removed at reduced pressure and the residue was dissolved in benzene and chromatographed on magnesol. About 30 mg. of a greasy solid was obtained which was sublimed, recrystallized from heptane, and resublimed; it melted at 99–100°, and was tetrahydrophthalide.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.40; H, 7.11.

The hydrazide[33] was formed from the lactone (90 mg.) by heating with 100% hydrazine hydrate on the steam-bath for three hours. The reaction mixture was dissolved in hot ethyl acetate; on cooling, 60 mg. of the hydrazide crystallized as thin white needles, m.p. 169–170°.

Anal. Calcd. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29. Found: C, 56.78; H, 8.45.

ROCHESTER, N. Y.

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[32] A. C. Cope and E. C. Herrick, THIS JOURNAL, **72**, 983 (1950).

[33] *Cf.* S. L. Friess, *ibid.*, **71**, 2571 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH, GOVERNMENT OF PAKISTAN, KARACHI, PAKISTAN,[1] AND THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO[2]]

Preparation of Deuterized Raney Nickel and Selective Deuteration of the Triple Bond[2]

BY N. A. KHAN[3]

RECEIVED OCTOBER 22, 1951

A procedure is described for the preparation of deuterized Raney nickel for use in deuterating the triple bond selectively to the double bond with a view to obtaining dideutero-olefinic compounds. A comparative study of hydrogenation and deuteration has been made, and selective deuteration is shown to be as effective as hydrogenation. The composition of the crude products obtained by the selective deuteration of the triple bond has been determined by an analytical scheme. A plausible explanation for the unusual selectivity of reduction of symmetrical acetylenic compounds by deuterium or hydrogen is presented. Evidence has been put forward for no exchange of deuterium gas with the hydrogen of saturated C-chain of methyl stearate over deuterized Raney nickel during the short period needed for selective deuteration. A method of preparation of a Raney nickel catalyst, designated W-8, containing much less hydrogen than other varieties, and free of lighter variety of the catalyst containing alumina, is also reported.

In a previous paper,[4] methyl stearolate was selectively deuterated to the corresponding olefinic compound with an assumption that the deuteration follows the same pattern of reaction as hydrogenation. No critical consideration was given to the identification of the different products formed by deuteration, nor were any conditions set up for this process. Furthermore, the Raney nickel catalyst, W-1,[5] used was not freed from the hydrogen adsorbed on the surface during preparation. Such retained hydrogen (125–250 ml. per 4 g. of catalyst)[6] would introduce some error in the extent of deuteration. The deuterium content of the purified methyl 9,10-dideutero-oleate reported[4] (only 90% of theory) confirms this fact.

In the present investigation a special procedure was developed to prepare deuterized Raney nickel, having deuterium adsorbed on its surface rather

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[1] Supported by grants from this department.

[2] Most of the experimental work was completed at the Ohio State University. Paper presented by title to the XII$^{\text{th}}$ International Congress, New York City, September, 1951.

[3] Up to July 1, 1951, Research Associate, Physiological Chemistry, the Ohio State University, and at present Research Fellow, Hormel Institute, University of Minnesota, Austin, Minnesota.

[4] N. A. Khan, F. E. Deatherage and J. B. Brown, *J. Am. Oil Chemists' Soc.*, **28**, 27 (1951).

[5] H. Adkins and L. W. Covert, THIS JOURNAL, **54**, 4116 (1932).

[6] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, *ibid.*, **65**, 1013 (943).

than hydrogen. The only method[7] which has been published for the preparation of deuterized Raney nickel consisted of treating W-2 Raney nickel[6,8] with deuterium oxide; the catalyst thus prepared was used in deuterolysis (*cf.* hydrogenolysis) experiments without supplementary deuterium gas, and presumably contained large amounts of adsorbed deuterium. Since the present study involved selective deuteration of the triple bond in an atmosphere of deuterium gas at room temperature (25–30°) and pressure (737–747 mm.), it seemed desirable to use a special type of Raney nickel catalyst. This catalyst was prepared free from alkali and alumina insofar as possible and with a minimum amount of hydrogen adsorbed on its surface, and was then deuterized by a procedure somewhat different from the one mentioned.[7]

The conditions for the selective deuteration were determined by a comparative study of hydrogenation and deuteration of a standard acetylenic compound, methyl stearolate,[4] as well as by the analyses of the respective crude hydrogenated and deuterated products thus obtained. The experiments were run at different pressures and with different amounts of catalysts and solvents.

Methods of purification of dideutero-olefinic compounds, methyl 9,10-dideutero-oleate, 9,10-dideutero-oleic acid and 9,10-dideutero-octadecene were devised, and the possibility of exchange of deuterium atoms with hydrogen atoms attached to a saturated paraffinic chain was investigated. The deuteration of a symmetrical acetylenic hydrocarbon, 9-octadecyne, showed a peculiar phenomenon of unusual selectivity of deuteration. The same selectivity was also noted by Max, *et al.*,[9] in hydrogenating the same compound, and by others[10,11] in the hydrogenation of other symmetrical acetylenic hydrocarbons. This suggested an explanation for such selectivity.

Results and Discussion

If the hydrogen adsorbed on Raney nickel is not displaced, it will compete with the deuterium used for the reduction of the triple bond. It appears that an equilibrium is usually established for the competitive reactions when the reduction of the triple bond is carried out in the presence of both hydrogen and deuterium.[4] The presence of alkali in the catalyst introduces to the system of deuteration a source of labile hydrogen which may help easy exchange of deuterium, and may cause error.[12,13]

For these reasons, the Raney nickel was prepared under special conditions of digestion and washing in order to free it completely from alkali and to have the least amount of hydrogen adsorbed on its surface. The low initial hydrogen content of the catalyst favored its replacement by deuterium. Furthermore, this catalyst, designated "ordinary" Raney nickel, was found to be more selective than W-1[5] and different from W-1, W-2 and W-3[14] as far as the reduction of the common substrates, stearolic acid and its methyl ester, was concerned. The last three catalysts contain very little alkali, but they possess different amounts of hydrogen and lighter nickel, containing alumina. The present catalyst with low hydrogen content and containing no free alkali or lighter nickel may be designated as W-8 Raney nickel.

Wilson[15] and Urry[16] have proved by their experiments that the C–D bond is stronger than the C–H bond. This, in conjunction with the heavier weight of the deuterium molecule and its higher bond energy, should mean a lower activity than that of the hydrogen molecule. The present experiments on catalytic deuteration and hydrogenation do not support this prediction, since the rates of the two processes are nearly the same. It may be that on the catalytic surface, such energy differences between deuterium and hydrogen are negligible. Deuteration and hydrogenation in the presence of platinum and palladium catalysts added further confirmation.

The curves in Fig. 1 show, within experimental errors, the similarity between deuteration and hydrogenation. Here deuterium seems to be more active at the start, gradually slowing down to the rate close to hydrogenation. In some other runs, closer similarity was also observed. The case for stearolic acid was included in order to show the lack of effect of the carboxyl group on hydrogenation in presence of the catalyst. But for the labile hydrogen, deuteration of the acetylenic acid might have been the same.

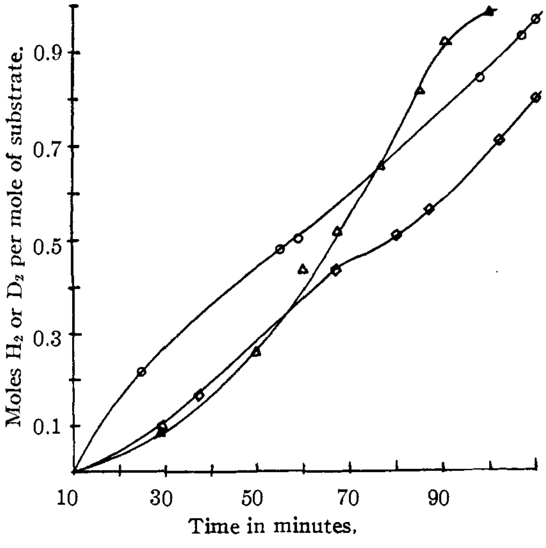

Fig. 1.—Rate of reduction: O, methyl stearolate with D_2; Δ, methyl stearolate with H_2; □, stearolic acid with H_2.

The experiments conducted with varying amounts of deuterized Raney nickel indicated that

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[7] H. T. Clarke, J. R. Johnson and R. Robinson, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p. 266.

[8] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[9] R. A. Max and F. E. Deatherage, *J. Am. Oil Chemists' Soc.*, **28**, 110 (1951).

[10] K. N. Campbell and M. J. O'Conner, THIS JOURNAL, **61**, 2897 (1939).

[11] M. C. Hoff, K. W. Greenlee and C. E. Boord, *ibid.*, **73**, 3329 (1951).

[12] R. Schoenheimer and D. Rittenberg, *J. Biol. Chem.*, **111**, 163 (1935).

[13] R. Schoenheimer and D. Rittenberg, *ibid.*, **111**, 169, 175 (1935).

[14] A. A. Pavlic and H. Adkins, THIS JOURNAL, **68**, 1471 (1946).

[15] C. L. Wilson, *J. Chem. Soc.*, 1550 (1936).

[16] W. H. Urry, Denver Symposium of Organic Chemistry Division, Am. Chem. Soc., 1951.

optimum selectivity and rate of deuteration occurred at room temperature (25–30°) and pressure (737–747 mm.), when the substrate contained 8 to 10% by weight of catalyst wet by solvent. The amount of solvent necessary for deuteration in the Joshel apparatus was found to depend on the size of the reaction vessel, the capacity of the magnetic stirrer to expose the nickel surfaces to deuterium gas and the solubilities of the substrates and the reaction products. Pressure reduction (30–40 lb./sq. in.) in the Parr machine proved to be unsatisfactory for deuteration. The Joshel system is not suitable for reduction at temperatures higher or lower than that of the room (25–30°). Under both these circumstances, the temperature and pressure of such a system cannot be kept uniform for good volumetric measurements of the gases, essential for selective deuteration. These results coincide with those in the case of hydrogenation in the presence of "ordinary" Raney nickel obtained before deuterization.

The composition of the crude products from the hydrogenation of methyl stearolate was calculated from their iodine and quantitative hydrogen absorption values, assuming that methyl stearate, methyl octadecenoate and methyl stearolate were the only components. The composition found was: methyl stearate, 3.7%; methyl stearolate, 2.1%; and methyl octadecenoate, 94.2%. The calculations were based on the fact that four atoms of hydrogen but only two atoms of iodine (Wijs, $^1/_2$-hour method) add to the acetylenic bond while two atoms of either hydrogen or iodine may be added to the ethylenic bond (*cf.* thiocyanogen number[17]).

Similarly the composition of the crude products obtained by the selective deuteration of methyl stearolate in the presence of deuterized Raney nickel was computed as methyl tetradeutero-stearate, 2.9%; methyl stearolate, 2.5%; and methyl 9,10-dideutero-octadecenoate, 94.6%. Infrared absorption measurements at 10.36 microns[18] indicated that the methyl octadecenoate consisted of 94% *cis*- and 6% *trans*-isomers. A similar analysis of methyl 9,10-dideutero-octadecenoate gave *cis* 95.8% and *trans* 4.2%.

The separation of the last trace of *trans*-isomer from *cis*-octadecenoic acid or its ester is very difficult. Preliminary experiments done with adsorption chromatography have shown promise of such separation. The details will be published elsewhere. However, in this investigation, very good results were obtained by low temperature crystallization.

Since the C–D bond is stable to hydrolytic conditions, it was possible to prepare the pure deutero acid from its ester. The deuteration of acetylenic acids was not attempted because of the presence of the labile hydrogen in the carboxyl group.

The experiments with saturated methyl stearate show that the exchange of hydrogen atoms attached to the paraffinic chain in the acetylenic compounds, with deuterium atoms, if there be any, during selective deuteration, is not fast enough to let deuterated C-atoms other than those related to the double bond accumulate to any appreciable extent.

Each of the deutero compounds was analyzed by micro-combustion,[19] and the collected water was decomposed into deuterium and hydrogen, which were subjected to mass spectrographic analysis to obtain the atom percentages of deuterium reported.

The deuteration of the symmetrical acetylenic hydrocarbon, 9,10-octadecyne, stops exactly after reduction of the triple bond to the double bond. This indicates that Ni forms a stronger association compound with the resultant double bond because of the equal distribution of electrons contributed by the balanced alkyl groups on either side. This association compound is probably not vulnerable to the attack by deuterium on the surface of the catalyst. On the other hand, the unequal distribution of electrons in the case of the olefinic compound obtained from the reduction of the unsymmetrical acetylenic compound, methyl stearolate, causes formation of nickel association compounds, vulnerable to deuterium attack. This will account for the further slow reduction beyond the olefinic stage in the latter, and no such reduction in the former. The same explanation will hold true for similar phenomena of hydrogenation.

All these ideas and experimental facts combine to indicate that the selective deuteration is as effective as the selective hydrogenation, if properly carried out.

The investigations including (a) isolation of isomeric compounds, especially positional, if they be formed, on selective deuteration, (b) mass-spectrographic analysis for studies on exchange of H-atoms in paraffinic chain with deuterium atoms, and (c) analyses on the crude products obtained on selective deuteration of various other acetylenic compounds are in progress and will be published later.

Experimental

Apparatus.—A modified Joshel semi-micro hydrogenation apparatus[20] with a 500-ml. graduated mercury-filled reservoir for deuterium gas was found to be very helpful for deuteration. One necessary change in the apparatus was the insertion of a pressure stopcock just above the outer standard joint, connecting the system to the reaction vessel. To facilitate manipulation when a deuterium reservoir with a capacity in excess of 500 ml. was required, the mercury in the reservoir was replaced with mineral oil which had been freed from labile hydrogen by long periods of impregnation with deuterium gas in presence of small amount of deuterized Raney nickel. By proper manipulations, deuterium gas could be introduced into the system as many times as necessary to selectively deuterate larger batches.

Materials.—Methyl stearolate and stearolic acid were prepared by the method of Khan, *et al.*[4] 9,10-Octadecyne was synthesized as described by Max and others.[9] Dioxane was purified.[21]

Preparation of "Ordinary" Raney Nickel.—Raney nickel was digested according to the procedure of Adkins,[5] except that the temperature was kept strictly between 100 and 105° all through the digestion. The washing procedure was a simplification of that used for the preparation of the W-6 catalyst,[22,23] avoiding hydrogen pressure and the closed system, but supplemented by several manual washings to

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(17) A.O.C.S. Official and Tentative Methods, Cd 2-38, page 5 (1946).

(18) D. Swern, H. G. Knight, O. D. Shreve and M. R. Heether, *J. Am. Oil Chemists' Soc.*, **27**, 17 (1950).

(19) J. B. Niederl and V. Niederl, "Organic Quantitative Micro-Analysis," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 108.

(20) L. M. Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943).

(21) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., New York, N. Y., 1941, p. 369.

(22) H. Adkins and H. R. Billica, This Journal, **70**, 695 (1948).

(23) H. Adkins and H. R. Billica, *Org. Syntheses*, **29**, 24 (1949).

remove the lighter catalyst particles. The catalyst was washed in an open cylinder provided with a stirrer and a water inlet reaching to the bottom of the cylinder. By proper choice of stirring speed and water flow the catalyst was suspended evenly in the lower $^3/_4$ of the water column in the cylinder. The wash water was simply allowed to flow over the top of the cylinder into the sink, carrying with it a certain amount of light catalyst particles. After about 36 liters of water had been flushed through the catalyst in a 24-hour period, the wash water was neutral. In order to remove additional quantities of light particles, the catalyst in the cylinder was agitated with a glass rod with one liter of water at a time and the cloudy water layer decanted. The process was continued until the top water column showed no turbidity (15 to 16 washings).

The alkali-free catalyst was washed once with 250 ml. of purified dioxane. It was then covered with 1.5 liters of solvent and distilled until the temperature of the vapor reached 101°. This "ordinary" Raney nickel was stored in a stoppered bottle full of dioxane.

Selectivity of "Ordinary" Raney Nickel.—Stearolic acid and its methyl ester were hydrogenated using the present catalyst as well as W-2 and W-3 and under otherwise identical conditions. In all cases where the new catalyst was used, hydrogenation fell down to an almost negligible rate after the triple bond had been reduced to the double bond. On the other hand, the other catalysts tended to completely saturate the triple bond, though at a lower rate when the double bond was involved. In addition, both W-2 and W-3 partly reduced the ester group of methyl stearolate.

Preparation of Deuterized Raney Nickel.—Twenty-five grams of the "ordinary" Raney nickel (still wet with dioxane) was washed once with a 25-ml. portion of dioxane by centrifugation and the nickel was then suspended in 10 ml. of 99.9% heavy water (D_2O) and allowed to stand in a stoppered tube for 48 hours. The nickel was occasionally stirred a few times throughout the equilibration period. It was then washed with three 25-ml. portions of dioxane and transferred to the reaction vessel of a Joshel apparatus (250-ml.) with the help of about 125 ml. of dioxane. To this catalyst in the reaction vessel was added 5 ml. of heavy water. The stopcock above the reaction vessel was then closed, the system evacuated and deuterium gas introduced. About 100 ml. of deuterium gas was collected in the 500-ml. reservoir. After closing all stopcocks to the outside, the stopcock over the reaction vessel was opened and the catalyst in dioxane was agitated in the presence of deuterium gas under slight pressure for two hours. The process was repeated three times, the system being flushed each time with dry oxygen-free nitrogen and filled with fresh deuterium. Nickel prepared in this manner was stored in purified dioxane containing a small amount of heavy water, and it appeared to give identical and satisfactory results over a period of more than four months, when moisture and oxygen were exclusively avoided by means of dry oxygen-free nitrogen gas.

Deuteration with Deuterized Raney Nickel.—Using the 250-ml. Joshel reaction flasks, quantities of solution greater than 100 to 125 ml. gave considerably lower rates of deuteration because of difficulties in suspending the catalyst in larger volumes of solution. Catalyst concentrations of 2, 8–10, 15, 25 and 50% by weight of substrates were used. The 8–10% level showed best results as far as selectivity, uniformity of rate and time required for deuteration were concerned. Since hydrogenations at pressures of 30, 40 and 45 p.s.i. gave poor yields of *cis*-form (70 to 80%) and required an excessive amount of gas, the Parr apparatus was found unsuitable for deuteration. The reaction temperatures cannot be conveniently varied with the Joshel apparatus; hence the effect of temperature on deuteration with the deuterized catalyst was not studied.

In selectivity the deuterized Raney nickel behaved the same as the "ordinary" catalyst from which it was prepared.

Comparative Rates of Deuteration and Hydrogenation.—The relative rates of reduction of methyl stearolate by deuterium and hydrogen and of stearolic acid by hydrogen under identical conditions in the presence of deuterized Raney nickel was studied as follows: in each case, 0.017 mole of substrate dissolved in dioxane was reduced in the presence of 10% by weight of catalyst with uniform stirring at room temperature (25–30°) and pressure (737–747 mm.). The absorption of hydrogen and deuterium plotted against time gave curves as shown in Fig. 1. The non-selective catalysts platinum[24] and palladium[25] were subjected to the same treatments using the appropriate amounts of catalyst. The adsorption of both hydrogen and deuterium by the substrate was very fast for platinum without any break after reduction of the triple bond to the double bond. Palladium showed some selectivity, but much less than Raney nickel. Deuteration and hydrogenation were found to be very closely related as far as the rates of adsorption were concerned in the presence of these platinum and palladium catalysts.

Composition of the Crude Products from the Selective Deuteration and Hydrogenation of Methyl Stearolate.—4.25 grams of methyl stearolate dissolved in dioxane was allowed to absorb exactly one mole of hydrogen in the presence of "ordinary" Raney nickel (0.4 g.). After removal of the catalyst with a fine sintered glass funnel, the solvent was removed and the crude products were distilled under vacuum. The iodine number and hydrogen absorption of this crude material were determined. The same procedure was repeated in case of deuteration of methyl stearolate in presence of deuterized Raney nickel. The calculations were completed according to the scheme described previously.

Preparation of Pure Methyl 9,10-Dideutero-oleate.—The experiments on the purification of deutero-oleate from methyl stearolate showed that this latter impurity is very hard to separate. This led to an attempt to eliminate unreacted methyl stearolate (2.5 to 3.1% of the crude mixture obtained by deuteration) by "overdeuteration." This was accomplished by allowing the methyl stearolate to absorb 6% excess deuterium over the calculated amount necessary to convert it to the dideutero-compound.

The crude mixture, predominantly dideutero-oleate, was freed from the saturates, etc., by crystallization at −32° from 5% acetone solution. The filtrate was then slowly cooled to −45° and warmed back to about −36° in order to remove some crystalline products. The process was repeated, this time cooling down to −50° and warming back to about −36 to −38°. Methyl dideutero-oleate was then crystallized by cooling the final filtrate to −65°. The precipitated deutero-oleate was twice washed with the solvent at −65° and then distilled under vacuum, b.p. 173–174° at 1.8–2.0 mm.; iodine number, 84.9 (theory 85.23); $n^{20}\text{D}$ 1.45185; deuterium uptake in presence of deuterized Raney nickel, 1 mole; deuterium, 5.45 atom per cent. (theory 5.55).

Some traces of *trans*-form were found even in the purified methyl 9,10-dideutero-oleate by infrared absorption at 10.36 microns.

Preparation of Pure 9,10-Dideutero-oleic Acid.—Fifteen grams of methyl 9,10-dideutero-oleate was saponified with excess alcohol and potassium hydroxide after refluxing the mixture for three hours. After addition of some distilled water, the solution was acidified with 6 *N* HCl. The liberated acids were extracted with two portions of ether. The ether solution was washed free of acid, dried, and the solvent removed. The residue was distilled under vacuum, b.p. 185–186° at 1.8–2 mm., neut. equiv., 283.5; deuterium, 5.64 atom per cent. (theory 5.88).

Infrared absorption for C–D bond was found to be the same as reported before.[4]

Exchange of Deuterium Atoms with Hydrogen Atoms Attached to a Saturated Paraffinic Chain.—A very pure sample of methyl stearate, iodine number 0.20 and neut. equiv. 284.3, was crystallized three times at room temperature from acetone solution. This purified methyl stearate was dissolved in dioxane and shaken with hydrogen in the presence of platinum catalyst[24] for 6 hours. On removal of the catalyst, the methyl stearate was again crystallized twice from acetone solution at room temperature. Four grams of this methyl stearate was dissolved in dioxane (125 ml.), introduced into the reaction vessel of a Joshel apparatus with 0.4 g. of deuterized Raney nickel and shaken with deuterium gas for 1 hour (average period of time necessary to deuterate 4 g. of methyl stearolate selectively to methyl 9,10-dideutero-oleate) under the same conditions as are usually used for selective deuteration. On removal of the catalyst and the solvent, the residue was twice crystallized from the

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[24] R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Coll. Vol. I, 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 463–470.

[25] Busch and Stöve, *Ber.*, **49**, 1064 (1916).

purified dry ether (especially alcohol-free) at low temperature. The methyl stearate so obtained was subjected to infrared analysis. No absorption for CD, or for CD_2 was observed.

Selective Deuteration of 9-Octadecyne.—Five grams of 9-octadecyne was dissolved in 125 ml. of purified dioxane and subjected to deuteration in the presence of deuterized Raney nickel. The reaction was very selective and deuterium absorption stopped when 1 mole of deuterium was taken up. Even with platinum catalyst,[24] there was a sharp drop in the rate of deuterium uptake after 1 mole was used up. Four runs of selective deuteration were made and the products combined after removal of the catalyst. When the solvent was removed, the crude residue containing 9,10-dideutero-octadecene was dissolved in purified and dry ether to make a 10% solution. This solution was allowed to crystallize at about −40 to −45° in a period of 2 hours or more. On removal of the crop of crystals, the filtrate was again allowed to cool at about −45 to −50° and left at the same range for about two hours and then crystals were filtered off. After removing the solvent from the final filtrate, 9,10-dideutero-octadecene was distilled under vacuum, b.p. 140–142° at 2–3 mm., deuterium 5.32 atom per cent. (theory 5.55).

Acknowledgment.—The author gratefully acknowledges the kind coöperation of Dr. C. L. Wilson and his group of the Chemistry Department, the Ohio State University, in performing infrared analyses of different samples during the course of this investigation. He also wishes to thank Dr. K. W. Greenlee of the American Petroleum Institute, Ohio State University branch, for the supply of palladium catalyst, and Dr. F. E. Deatherage of the Agricultural Biochemistry Department for his kind help.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Preparation and Properties of 3,3,3-Trifluoro-1,2-epoxypropane[1]

BY E. T. McBEE AND THEODORE M. BURTON[1a]

RECEIVED SEPTEMBER 4, 1951

The reduction of 3-bromo-1,1,1-trifluoropropanone with lithium aluminum hydride produced 3-bromo-1,1,1-trifluoro-2-propanol with only limited replacement of the bromine atom. When 3-bromo-1,1,1-trifluoro-2-propanol was treated with aqueous sodium hydroxide at low temperature, hydrolysis of the bromine atom produced 3,3,3-trifluoro-1,2-propanediol. At higher temperatures, dehydrohalogenation of the bromohydrin produced 3,3,3-trifluoro-1,2-epoxypropane. The polyfluorinated epoxide was not as reactive as 1,2-epoxypropane probably due to the stabilizing effect of the electronegative trifluoromethyl grouping. It was found possible to open the ring by both acid- and base-catalyzed hydrolysis to form the corresponding glycol.

Discussion

The bromine atom of 3-bromo-1,1,1-trifluoropropanone has been found to be so reactive[2] that some doubt was raised as to whether it would be possible to reduce the carbonyl group without replacing the bromine atom. However, it was found possible to reduce 3-bromo-1,1,1-trifluoropropanone to the corresponding bromohydrin in 48.8% yield using the very mild Meerwein–Ponndorf–Verley reduction,[3] but the reaction required prolonged rectification which made it a very time-consuming synthesis.

Trevoy and Brown[4] used lithium aluminum hydride to reduce *p*-bromophenacyl bromide to α-(*p*-bromophenyl)-ethanol. It was thought that the loss of bromine might be explained by the fact that they used excess metal hydride in their reduction. The corresponding bromohydrin was later prepared in 69% yield from *p*-bromophenacyl bromide.[5] In the present research it was similarly found that straightforward reduction of the carbonyl group of 3-bromo-1,1,1-trifluoropropanone proceeds more rapidly than the reductive replacement of the halogen of either the haloketone or of the halohydrin.

Sodium borohydride is a milder reducing reagent than lithium aluminum hydride and can be used in either water or methanol solution. It was thought that sodium borohydride might give better yields of the bromohydrin when used with the very reactive 3-bromo-1,1,1-trifluoropropanone. Though reduction did occur, the yield was only about half that obtained with lithium aluminum hydride. The probable reason for the lowered yield is the formation of a stable hydrate or hemiacetal when 3-bromo-1,1,1-trifluoropropanone is placed in water or alcohol. With no free carbonyl grouping present, the reduction was probably made more difficult. Since anhydrous ether was used as solvent with lithium aluminum hydride, no masking of the carbonyl group occurred.

With the successful synthesis of the bromohydrin, it became possible to study the preparation of polyfluorinated epoxy derivatives. The dehydrohalogenation of the bromohydrin to produce 3,3,3-trifluoro-1,2-epoxypropane was successful using the method of Abderhalden and Eichwald.[6] The principal side reaction involved the hydrolysis of the bromine atom to produce the corresponding polyfluorinated glycol. Lower temperatures, dilute solutions and longer contact time favored the formation of the glycol at the expense of the epoxide. No dehydrohalogenation to produce 1,1,1-trifluoropropanone was noted when the basic solution was acidified. It was impossible to extract the glycol from a basic solution with ether, for the

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(1) This paper contains material abstracted from the thesis of Theodore M. Burton submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1951.

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